Supporting information

Real-Time Monitoring of Formation and Dynamics of Intra- and Interchain Phases in Single Molecules of Polyfluorene

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Figure S1. a) - c) Fluorescence images of low M_w PFO dispersed in a PS thin film before (a) and under SVA with toluene for 15 min (b) and 2 hours (c). The color lines in b) and c) represent traces of the diffusing molecules; d) - f) Numbers of emitting spots (PFO chains) found in fluorescence images from 20 individual locations inside the samples shown in a) - c); g) - j) Fluorescence intensity distributions of single PFO chains analyzed from the 20 individual locations inside the samples shown in a) - c).

Analysis of the fluorescence images

The images in Fig. S1a-c show a distribution of intensities in the from of bright and dark fluorescence spots. The fluorescence spectra from both the bright and darker spots are consistent with PFO spectra and prove that the fluorescence originates from PFO. The differences in the brightness can be explained by the large molecular weight distribution. From the values of M_w and PDI it is possible to estimate the relative width $\sigma_n/M_n=1.56$, where σ_n is a standard deviation. This ratio is much larger than the similar ratio $\sigma_I/\langle I_F \rangle$ obtained from the distribution of fluorescence intensity in, *e.g.*, Fig. S1g, which is on the order of 0.3 ~ 0.4. Thus, the molecular weight distribution is much larger than the similar the corresponding fluorescence intensity distribution. Further, the intensity shows a single-component distribution pointing to only the molecular weight distribution as the factor for the varying brightness.



Figure S2. a) Fluorescence spectra of drop-cast films of PS doped with ensemble-level concentrations (on the order of 10^{-6} M) of low M_w PFO before SVA and during SVA for different time periods. The SVA times are shown in the legend and the lines are distinguished by the corresponding colors. b) Same as a) for the high M_w PFO.



Figure S3. a) 2D fluorescence spectral plot of time evolution of a single low M_w PFO chain spectra, showing spontaneous switching between the glassy phase and the aggregation-induced green emission band; b) - d) Stationary spectra from the same PFO chain obtained from the time intervals indicated by the arrows in a).



Figure S4. a) 2D fluorescence spectral plot of time evolution of a single low M_w PFO chain, showing spontaneous switching from β -phase to glassy phase emission; b), c) Stationary spectra from the same PFO chain obtained from the time intervals indicated by the arrows in a).



Figure S5. a), b) Fluorescence spectra from single high M_w PFO chains after 15 min SVA, showing the glassy phase (a) or mixed glassy and β -phase character (b); c) 2D fluorescence spectral plot of time evolution of a single high M_w PFO chain spectra, showing spontaneous switching between the glassy phase and the aggregation-induced green emission band; d), e) Stationary spectra from the same PFO chain obtained from the time intervals indicated by the arrows in c).



Figure S6. a) Distribution of the phonon energies of the 0-1 spectral line obtained from the fitting procedure as a difference between the 0-0 and 0-1 peaks; the energies correspond approximately to several Raman modes in the 1100 cm⁻¹ - 1400 cm⁻¹ range; b) Reorganization energy SE_p plotted against the 0-0 peak energy. Black symbols - SVA for 2 hours, red symbols - SVA for 4 hours.



Figure S7. Linewidths of the 0-0 and 0-1 fluorescence peaks plotted versus the 0-0 peak energy for the high M_w PFO single chains in the β -phase spectral region.